PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference HYI-01-101-P	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/US04/23707	International filing date *(day/month/year)* 22 July 2004 (22.07.2004)	Priority date *(day/month/year)* 23 July 2003 (23.07.2003)
International Patent Classification (IPC) or national classification and IPC IPC(7): C01B 3/16 and US Cl.: 252/373; 423/650,651,652,655		
Applicant HYRADIX, INC		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 5 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) _____ , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).
4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18 May 2005 (18.05.2005)	02 September 2005 (02.09.2005)
Name and mailing address of the IPEA/ US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Stan Silverman DEBORAH A. THOMAS PARALEGAL SPECIALIST Telephone No. 703-308-0661 ~~GROUP 1500~~

Form PCT/IPEA/409 (cover sheet)(April 2005)

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US04/23707

Box No. I Basis of the report

1. With regard to the **language**, this report is based on:
   - ☒ the international application in the language in which it was filed.
   - ☐ a translation of the international application into English, which is the language of a translation furnished for the purposes of:
     - ☐ international search (under Rules 12.3 and 23.1(b))
     - ☐ publication of the international application (under Rule 12.4(a))
     - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:
   - ☐ the international application as originally filed/furnished
   - ☒ the description:
     pages 1-20 and 24-26 as originally filed/furnished
     pages* 21-23,23/1 received by this Authority on 18 May 2005 (18.05.2005)
     pages* NONE received by this Authority on _____
   - ☒ the claims:
     pages 27-32 as originally filed/furnished
     pages* NONE as amended (together with any statement) under Article 19
     pages* NONE received by this Authority on _____
     pages* NONE received by this Authority on _____
   - ☒ the drawings:
     pages 1 and 3-5 as originally filed/furnished
     pages* 2 received by this Authority on 18 May 2005 (18.05.2005)
     pages* NONE received by this Authority on _____
   - ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages _____
   - ☐ the claims, Nos. _____
   - ☐ the drawings, sheets/figs _____
   - ☐ the sequence listing (*specify*): _____
   - ☐ any table(s) related to the sequence listing (*specify*): _____

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages _____
   - ☐ the claims, Nos. _____
   - ☐ the drawings, sheets/figs _____
   - ☐ the sequence listing (*specify*): _____
   - ☐ any table(s) related to the sequence listing (*specify*): _____

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US04/23707

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-29	YES
	Claims NONE	NO
Inventive Step (IS)	Claims 1-29	YES
	Claims NONE	NO
Industrial Applicability (IA)	Claims 1-29	YES
	Claims NONE	NO

2. Citations and Explanations (Rule 70.7)

Claims 1-29 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest
For claims 1-23 that a) generating hydrogen at a rate within a first rate range sufficient to accumulate hydrogen in a reservoir; b) upon a predetermined first amount of hydrogen being accumulated in the reservoir, changing the rate of hydrogen generation to a rate within a second range insufficient to maintain the first amount of hydrogen in the reservoir; and c) upon a predetermined second mount of hydrogen being in the reservoir, said second amount being less than the first amount, changing the rate of hydrogen generation to a rate within said first rate range.

For claims 24-29, changing the rate of hydrogen production from a first rate to a second rate and maintaining a substantially constant pressure swing cycle time for the adsorption at each such rate and varying the purity of the purified hydrogen stream.

Claims 1-29 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

---------- NEW CITATIONS ----------

use for the hot water. The cooled shift effluent passes via line 140 to compressor 142. As shown, thermocouple T3 detects the temperature of the cooled shift effluent.

[0073] The compressed shift effluent is passed via line 144 to pressure swing absorber 146. The desorption cycle gas from the pressure swing absorber is passed via line 152 to combustor 116. The purified hydrogen product stream is then passed via line 148 to reservoir 150. Reservoir 150 is equipped with sensor H1 which determines the amount of hydrogen contained in the reservoir.

[0074] Hydrogen is withdrawn from reservoir 150 via line 154, and hydrogen, as needed, can pass via line 156 to fuel cell 158, and hydrogen, as needed can pass to supply point 160. Fuel cell 158 also receives water from line 108 via line 162 and air from line 112. As shown, fuel cell controller 164 is provided to control the feed to and operation of the fuel cell. Electrical power is withdrawn from fuel cell 158 via cable 166. A portion of the generated electricity can be used to meet the electrical demands of the apparatus. Since the hydrogen fed to the fuel cell is highly pure, it can be recycled and essentially no anode purge gas is generated. A cathode waste gas containing nitrogen and unreacted oxygen is exhausted from fuel cell 158 via line 168 and is passed to heat exchanger/combustor 116 as an additional source of oxygen and as a temperature moderator. Alternatively, the cathode waste gas may be exhausted.

[0075] Figure 2 schematically diagrams the control of the apparatus of Figure 1. Numeral 200 generally indicates a computer-based control processor. Sensor H1 is in communication with the fuel supply routine 202 of the processor. The fuel supply routine 202 provides primary control to valve F1 which establishes the flow rate of fuel to be reacted in reformer 106. Based upon the signal from sensor H1, the fuel supply routine 202 will direct valve F1 to be position to provide fuel flow for a net hydrogen make or a net hydrogen depletion. The fuel supply routine 202 will also set various other valves and operations (ancillary) in the hydrogen generator. If the reforming involves a partial oxidation, the fuel supply routine 202 will set valve A1 for the flow of air to the reformer based upon the expected amount of air to be needed. As the composition of the fuel changes or the reforming catalyst deactivates, the predetermined amount of air predetermined by fuel supply routine 202 may be inappropriate to maintain reformer within the desired temperature range. Hence, thermocouple T1 provides to subroutine 204 the

reforming temperature that can then fine tune valve A1 to maintain a temperature within the sought range.

[0076] Fuel supply routine 202 also sets valve F2 to provide the expected amount of fuel to heat exchanger/combustor 116 for providing heat for reforming. Again, changing fuel compositions, reforming catalyst deactivation, changes in the volume of cathode waste gas, fouling of the heat transfer surfaces and the like can occur and the actual quantity heat being transferred to the incoming air for reforming may be different than that predetermined by fuel supply routine 202. The temperature of the reforming will reflect the actual heat being transferred and thus subroutine 204 can fine tune the flow through valve F2 based upon the signal from thermocouple T1 to bring the reforming temperature within the desired range.

[0077] Fuel supply routine 202 also sets valve A2 for the air passing to heat exchanger/combustor 116. Typically, the predetermined amount of air for combustion can be in a significant excess of that required stoichiometrically and hence no fine tuning of this flow is usually done. Similarly, water is provided to reformer 106 in a substantial excess and the setting established by fuel supply routine 202 generally requires no fine tuning.

[0078] Fuel supply routine 202 also sets valve W2 for the supply of water for cooling the reformate and providing water for the shift reaction. As shift reactions are dependent upon temperature, thermocouple T2 is in communication with subroutine 206 for fine tuning this flow of water. Fuel supply routine 202 sets valve W3 to control the flow of water to cooler/condenser 132. The temperature of the cooling water may change and the heat exchange surfaces may become fouled. Accordingly, subroutine 208 is provided, which in communication with thermocouple T3, fine tunes the flow of cooling water by further adjusting valve W3 such that the temperature of the shift effluent is within the desired range.

[0079] Fuel supply routine 202 is used to control the cycle times (PSACT) for pressure swing adsorber 146. For simplifying control of the pressure swing adsorber, the cycle times, predetermined for each net hydrogen make rate and each net hydrogen depletion rate, will be conservative. Thus, the same cycle times will be acceptable as the reforming catalyst and water gas shift catalyst approach the end of their useful lives. Alternatively sensors could be used to determine the composition of the purified hydrogen product and an additional subroutine provided to fine tune the pressure swing adsorber cycle times.

[0080] As stated above, subroutines 204, 206 and 208 are used to fine tune the position of valves to maintain a temperature condition within a predetermined range. As the process uses a pressure swing absorber to purify the hydrogen, significant variations in reformate compositions and water gas shift effluent compositions can be tolerated while still providing hydrogen at acceptable purity levels. Hence the ranges can be relatively broad, e.g., as great as 10°C or more. Thus the fine tuning can occur relatively easily and without a cyclic overshooting and undershooting of the target range. A failure of any of T1, T2 and T3 or the subroutines with which they communicate will not necessarily be fatal to the continued operation of the apparatus as fuel supply routine 202 provides the coarse settings.

[0081] Figure 4 depicts a four bed pressure swing adsorber useful for purifying hydrogen produced by autothermal reforming with air. A feed containing hydrogen, nitrogen, argon, water, carbon dioxide, carbon monoxide and any unreacted hydrocarbon-containing feedstock is passed via line 402 to one of vessels 404, 406, 408 and 410 which is in the adsorption phase of the cycle. Each of the vessels has a valve, 404A, 406A, 408A and 410A, respectively, to permit flow of the feed to the vessel at one end. Each of the vessels at the same end is in fluid communication with a purge header 412 through valves 404B, 406B, 408B and 410B. Each of the vessels is in fluid communication at the opposing end with purified product header 414 through valves 404E, 406E, 408E and 410E. Also on said opposing end, each vessel is in fluid communication with pressurization header 415 through valves 404F, 406F, 408F, and 410F. Further on said opposing end, each vessel is in fluid communication with provide equalization / provide purge header 416 through valves 404C, 406C, 408C, and 410C. Finally on said opposing end, each vessel is in fluid communication with receive equalization / receive purge header 417 through valves 404D, 406D, 408D, and 410D.

[0082] A proportional control valve 431 is provided on the equalization / purge header in order to control the rate of pressure change in the beds during provide purge and provide equalization steps. An additional proportional control valve 432 is provided on the pressurization header in order to control the rate of pressurization. A further control valve 430 is provided on the tail gas line 412 in order to control the rate of blowdown.

[0083] Each of the vessels is filled with adsorbent, e.g., a granular activated carbon adsorbent for about 30 volume percent of the bed closest to the feed inlet and the remainder being a beaded lithium exchanged X molecular sieve.

[0084] For the bed undergoing adsorption, its valves A and E are open and purified hydrogen product stream enters header 414. Once a bed goes off the adsorption step of the

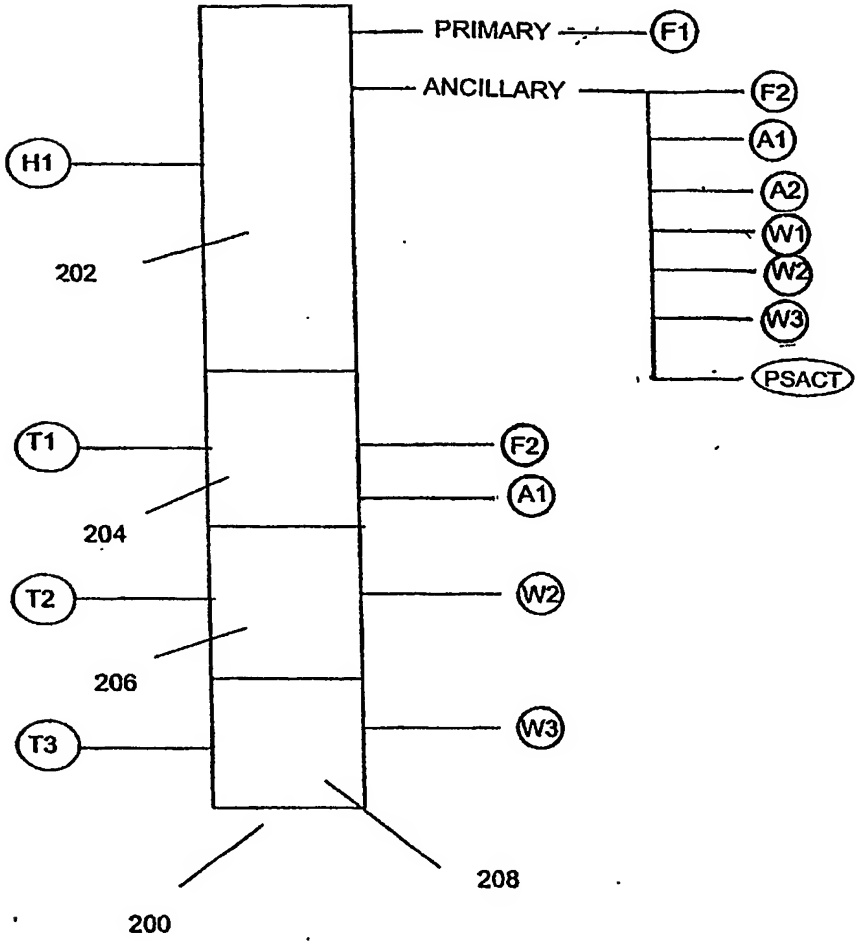
PRIMARY
F1
ANCILLARY
F2
A1
A2
W1
W2
W3
PSACT
H1
202
T1
F2
A1
204
T2
W2
206
T3
W3
208
200

FIGURE 2